StatMech questions: Debye Hückel Theory

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1 Expression of potential around ions in electolyte

Let we have system of N spherical charged particles of the same size. We will consider particles to be a hard spheres of diameter a. Let $\mathbf{r_1}, \ldots, \mathbf{r_N}$ are the coordinates of the particles, $q_1, ..., q_N$ are charges of the particles. Let there are m different particle species in the system:

$$\forall i \in \{1, \ldots, N\} \qquad q_i \in \{Q_1, \ldots, Q_m\} \tag{1}$$

The system is electroneutral:

$$\sum_{i=1}^{N} q_i = 0 \tag{2}$$

The total potential energy of the system is:

$$U_N(\mathbf{r^N}) = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N} \frac{q_i q_j}{\varepsilon|\mathbf{r_i} - \mathbf{r_j}|} + \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N} u(|\mathbf{r_i} - \mathbf{r_j}|) \tag{3}$$

where
$\mathbf{r^N} = \mathbf{r_1}, \ldots, \mathbf{r_N}$ are coordinates of the particles
$u(|\mathbf{r_i} - \mathbf{r_j}|)$ is potential of hard sphere interactions
ε is dielectrical constant

The potential at the point $\mathbf{r}$ is the sum of potentials of all particles:

$$\psi(\mathbf{r}) = \sum_{i=1}^{N} \frac{q_i}{\varepsilon|\mathbf{r_i} - \mathbf{r_j}|} \tag{4}$$

Let's consider the mean potential at the point $\mathbf{r}$ given a particle at the point $\mathbf{r_1}$

$$\langle \psi(\mathbf{r}|\mathbf{r_1}) \rangle = \frac{\int \psi(\mathbf{r}) e^{-\beta U_N} d\mathbf{r^{N-1}}}{\int e^{-\beta U_N} d\mathbf{r^{N-1}}} \tag{5}$$

where
$\beta = \frac{1}{k_B T}$ is inverse temperature
$d\mathbf{r^{N-1}} = d\mathbf{r_2} \ldots d\mathbf{r_N}$

Potential (4) should obey Poisson equation:

$$\nabla^2 \psi(\mathbf{r}) = -\frac{4\pi q(\mathbf{r})}{\varepsilon} \tag{6}$$

where
$\nabla^2 \psi = (\frac{\partial^2 \psi}{\partial x}, \frac{\partial^2 \psi}{\partial y}, \frac{\partial^2 \psi}{\partial z})$
$q(\mathbf{r})$ is charge density at the point $\mathbf{r}$

Putting this to the (5) we obtain:

$$\nabla^2\langle\psi(\mathbf{r}|\mathbf{r_1})\rangle = \frac{\displaystyle\int \nabla^2\psi(\mathbf{r})e^{-\beta U_N}d\mathbf{r^{N-1}}}{\displaystyle\int e^{-\beta U_N}d\mathbf{r^{N-1}}} = \frac{\displaystyle\int -\frac{4\pi q(\mathbf{r})}{\varepsilon}e^{-\beta U_N}d\mathbf{r^{N-1}}}{\displaystyle\int e^{-\beta U_N}d\mathbf{r^{N-1}}} = -\tfrac{4\pi}{\varepsilon}\langle q(\mathbf{r}|\mathbf{r_1})\rangle \tag{7}$$

where

$q(\mathbf{r}) = \sum_{i=1}^{N} q_i\delta(\mathbf{r_i})$ is a charge density at a point $\mathbf{r}$

$\langle q(\mathbf{r}|\mathbf{r_1})\rangle$ is the mean charge density given the first particle at coordinates $\mathbf{r_1}$

Let's consider, the first particle belongs to the 1st species (that means, the charge of first particle $q_1 = Q_1$). Mean charge at the point is the sum of densities of each particle species multiplied by the charge of that species:

$$\langle q(\mathbf{r}|\mathbf{r_1})\rangle = \sum_{s=1}^{m} Q_s\rho_{1s}(\mathbf{r}|\mathbf{r_1}) = \sum_{s=1}^{m} Q_s n_s g_{1s}(\mathbf{r}|\mathbf{r_1}) \tag{8}$$

where

Q_s is charge of s-th particle species

$\rho_{1s}(\mathbf{r}|\mathbf{r_1})$ is conditional number density of species s around the first particle at the position $\mathbf{r_1}$

$n_s = \frac{N_s}{V}$ is number density of s-th species

$g_{1s}(\mathbf{r}|\mathbf{r_1})$ is pair correlation function between particle species 1 and s around the first particle at the point r_1.

If we consider an isotropic case, correlation function $g_{1s}(\mathbf{r}|\mathbf{r_1})$ depends only on the dirrefence of coordinates, and we may put the first particle to the origin and define a new function:

$$g(\mathbf{r'}) \equiv g(\mathbf{r} - \mathbf{r_1}|\mathbf{0}) = g(\mathbf{r}|\mathbf{r_1}) \tag{9}$$

Now, let's assume function $g(\mathbf{r})$ has a view:

$$g_{1s}(\mathbf{r}) = \begin{cases} 0 & r < a \\ e^{-\beta Q_s\langle\psi(\mathbf{r}|\mathbf{r_1})\rangle} = e^{-\beta Q_s\phi_1(\mathbf{r})} & r \geqslant a \end{cases} \tag{10}$$

where $\phi_1(\mathbf{r}) \equiv \langle\psi(\mathbf{r}|\mathbf{r_1})\rangle$

In this consideration we think about the particles 2,3,...,N as about the ideal gas, distriuted accordig to the maxwellian low in the potential field around the first particle. Putting (10) to (8) we obtain:

$$\langle q(\mathbf{r}|\mathbf{r_1})\rangle = \begin{cases} 0 & r < a \\ \displaystyle\sum_{s=1}^{m} n_s Q_s e^{-\beta Q_s\phi_1(\mathbf{r})} & r \geqslant a \end{cases} \tag{11}$$

Putting (11) to the Poisson equation (7) we obtain Poisson-Boltzman equation:

$$\begin{cases} \nabla^2\phi_1(\mathbf{r}) = 0 & r < a \\ \nabla^2\phi_1(\mathbf{r}) = -\dfrac{4\pi}{\varepsilon}\displaystyle\sum_{s=1}^{m} n_s Q_s e^{-\beta Q_s\phi_1(\mathbf{r})} & r \geqslant a \end{cases} \tag{12}$$

The system is electroneutral. So, potential $\phi_1(\mathbf{r})$ should vanish at infinity. We should also require continuity of potential $\phi_1(\mathbf{r})$ and of its normal derivative $\frac{\partial \phi_1}{\partial \mathbf{n}}$ on the sphere $r = a$:

$$\begin{cases} \nabla^2 \phi_1(\mathbf{r}) = 0 & r < a & (a) \\ \nabla^2 \phi_1(\mathbf{r}) = -\dfrac{4\pi}{\varepsilon} \displaystyle\sum_{s=1}^{m} n_s Q_s e^{-\beta Q_s \phi_1(\mathbf{r})} & r \geqslant a & (b) \\ \phi_1(\mathbf{r})\big|_{|\mathbf{r}|=a-0} = \phi_1(\mathbf{r})\big|_{|\mathbf{r}|=a+0} & & (c) \\ \dfrac{\partial \phi_1}{\partial \mathbf{n}}\bigg|_{|\mathbf{r}|=a-0} = \dfrac{\partial \phi_1}{\partial \mathbf{n}}\bigg|_{|\mathbf{r}|=a+0} & & (d) \\ \phi_1(\mathbf{r})\big|_{|\mathbf{r}|=\infty} = 0 & & (e) \end{cases} \tag{13}$$

where $\mathbf{n}$ is normal vector to the sphere of radius a.

We may solve solve equations (13a) and (13b) separateley, and then connect solutions to satisfy conditions (13c) and (13d)

Equation (13b) is nonlinear and is hardly solved. However, it might be linearized by using Teilor expansion of the exponent:

$$\sum_{s=1}^{m} n_s Q_s e^{-\beta Q_s \phi_1(\mathbf{r})} = \sum_{s=1}^{m} n_s Q_s - \beta \sum_{s=1}^{m} n_s Q_s^2 \phi_1(\mathbf{r}) + O(\phi_1^2(\mathbf{r})) \tag{14}$$

If we consider potential $\phi_1(\mathbf{r})$ to be small enough, we may omit high-order terms in (14). Putting this expression to (13b) we have:

$$\nabla^2 \phi_1(\mathbf{r}) = -\frac{4\pi}{\varepsilon} \left(\sum_{s=1}^{m} n_s Q_s - \beta Q_s \phi_1(\mathbf{r}) \right) \tag{15}$$

Due to electroneutrality, the first summations at the right side vanishes:

$$\sum_{s=1}^{m} n_s Q_s = 0 \tag{16}$$

And we have:

$$\nabla^2 \phi_1(\mathbf{r}) = \kappa^2 \phi_1(\mathbf{r}) \tag{17}$$

where

$$\kappa^2 = \frac{4\pi\beta}{\varepsilon} \sum_{s=1}^{m} n_s Q_s^2 \tag{18}$$

Since the function $\phi_1(\mathbf{r})$ is spherically simmetric, we may use spherical coordinates, and for equation (17) obtain:

$$\frac{1}{r^2} \frac{d}{dr^2} \left(r^2 \frac{d\phi_1}{dr} \right) = \kappa^2 \phi_1(r) \qquad r > a \tag{19}$$

The general solution of this equation is:

$$\phi_1(r) = \frac{A_1 e^{-\kappa r}}{r} + \frac{B_1 e^{-\kappa r}}{r} \qquad r > a \tag{20}$$

where A_1,B_1 are some constants

To satisfy (13e) solution should vanish at infinity we have to put $B_1 = 0$. We have:

$$\phi_1(r) = \frac{A_1 e^{-\kappa r}}{r} \tag{21}$$

Now, we may solve equation (13a). In spherical coordinates it is:

$$\frac{1}{r^2}\frac{d}{dr^2}\left(r^2\frac{d\phi_1}{dr}\right) = 0 \qquad 0 < r < a \tag{22}$$

The general solution of this equation is

$$\phi_1 = \frac{A_2}{r} + B_2 \qquad 0 < r < a \tag{23}$$

where A_2,B_2 are constants

We may find the constant A_2 using the Gauss' law. According to it, the electric flux through any closed surface is proportional to the enclosed electric charge .

$$\int_S \mathbf{E}(\mathbf{r}) \cdot d\mathbf{S} == \int_S \nabla\phi_1(\mathbf{r}) \cdot d\mathbf{S} = \frac{4\pi q}{\varepsilon} \tag{24}$$

where
S is some closed surface
$\mathbf{E}(\mathbf{r}) = -\nabla\phi_1(\mathbf{r})$ is electrical field

$d\mathbf{S}$ is tangent vector, proportional to the infinitesmal surface element dS.

For the sperical symetrical potential $\phi_1(r)$ and sphere $|\mathbf{r}| = r_0$ we have

$$4\pi r_0^2 \left(-\partial\phi_1\partial r\right)_{r_0} = \frac{4\pi q_1}{\varepsilon} \tag{25}$$

Putting (23) to (25) we obtain:

$$A_2 = \frac{q_1}{\varepsilon} \tag{26}$$

and

$$\phi_1(r) = \frac{q_1}{\varepsilon r} + B_2 \qquad 0 < r < a \tag{27}$$

Putting equations (21) and (27) to the conditions (13c) and (13d) we have

$$\begin{cases} \dfrac{A_1}{a}e^{-\kappa a} = \dfrac{q_1}{\varepsilon a} + B_2 \\ \dfrac{A_1}{a^2}e^{-\kappa a} + \dfrac{\kappa A_1}{a}e^{-\kappa a} = \dfrac{q_1}{\varepsilon a^2} \end{cases} \tag{28}$$

The solution of this system of two linear equations is:

$$A_1 = \frac{q_1 e^{\kappa a}}{\varepsilon(1+\kappa a)} \qquad B_2 = -\frac{q_1\kappa}{\varepsilon(1+\kappa a)} \tag{29}$$

Putting these constants to (21), (27) we find the expression for the potential:

$$\phi_1(r) = \begin{cases} \dfrac{q_1}{\varepsilon r} - \dfrac{q_1\kappa}{\varepsilon(1+\kappa a)} & 0 < r < a \\ \dfrac{q_1 e^{-\kappa(r-a)}}{\varepsilon(1+\kappa a)} & r > a \end{cases} \tag{30}$$

where κ is defined by (18)

2 Practical part

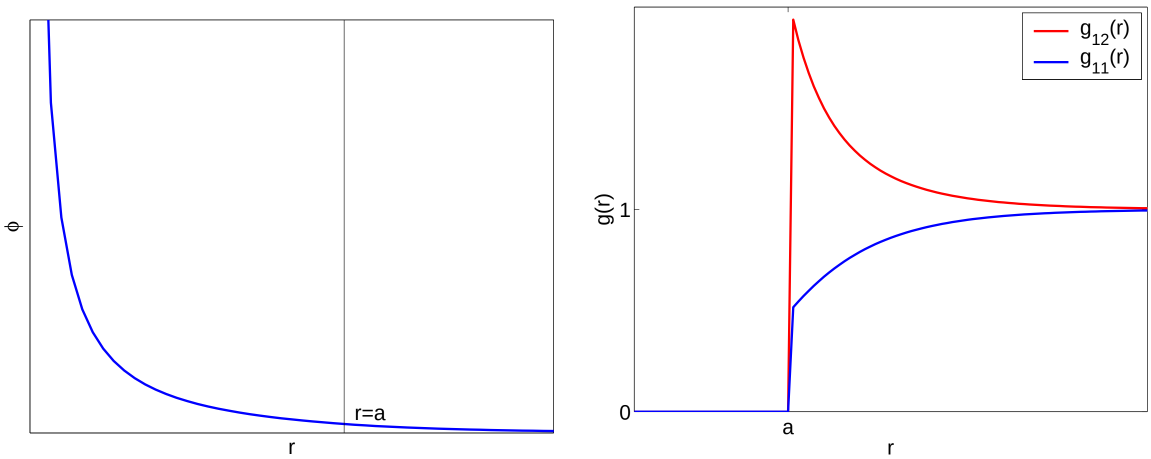
For the two-component system with charges $+-1$, potential (30) is:

$$\phi_1(r) = \begin{cases} \dfrac{1}{\varepsilon r} - \dfrac{\kappa}{\varepsilon(1+\kappa a)} & 0 < r < a \\ \dfrac{e^{-\kappa(r-a)}}{\varepsilon(1+\kappa a)} & r > a \end{cases} \tag{31}$$

Putting this potential to the expression for the RDF function (10) we have:

$$g_{1s}(\mathbf{r}) = \begin{cases} 0 & r < a \\ e^{c\frac{\beta}{\varepsilon(1+\kappa a)}e^{-\kappa(r-a)}} & r \geqslant a \end{cases} \tag{32}$$

where
$c = +1$ for ions with different charges (RDFs $g_{12}(r)$ and $g_{21}(r)$)
$c = -1$ for ions with a same charge (RDFs $g_{11}(r)$ and $g_{22}(r)$)
These results are graphically presented at the figure 1



(a) Potential around ion

(b) RDF functions for the ions with different charges and the same charge

Figure 1: Potential and RDF's around ion